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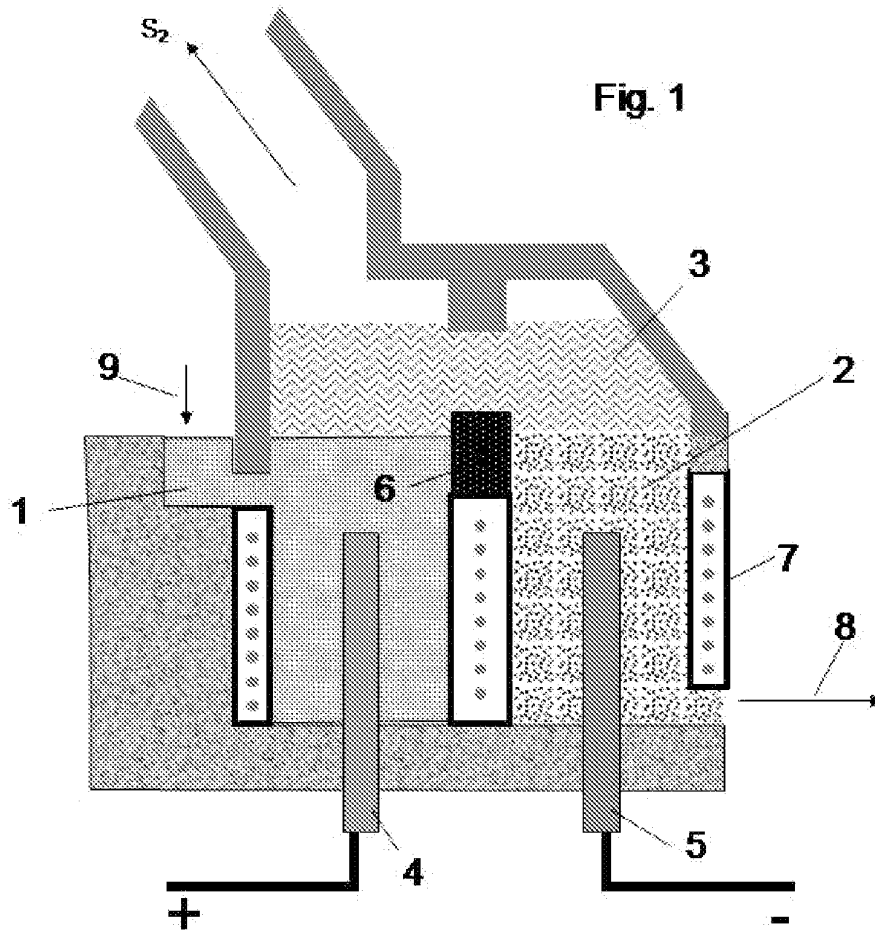
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(54) **Process for the production of copper from sulphide compounds**

(57) The present invention is related to a process for the production of copper from a matte comprising Cu_2S being in the form of a liquid placed in an electrolytic cell

at the positive pole wherein the electrolyte comprises molten salt, and wherein liquid copper is produced at the negative pole.



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Description

Field of the Invention

[0001] The present invention is related to a process for the production of copper and sulphur from copper sulphide compounds.

State of the Art

[0002] The pyrometallurgical routes to produce copper from sulphide containing raw or secondary materials consist generally of two main steps described hereafter.

[0003] In a first step the materials are melted in such conditions that a sulphide melt is produced, called matte (composition belonging mainly to the binary Cu_2S - FeS system), which is liquid at working temperature and separates from the slag. In this step a certain amount of iron sulphide is transferred to the slag in the form of iron oxide so that the resulting matte is enriched in copper. During the melting which is generally a continuous process SO_2 is produced and generally used to produce sulphuric acid.

[0004] A matte is generally defined, in the field of pyrometallurgy, as the molten metal sulfide phases typically formed during smelting of copper, nickel, and other base metals.

[0005] In a second step called matte converting, an oxidation atmosphere is produced by air, enriched air or pure oxygen in order to transform copper sulphide into copper and iron sulphide into iron oxide dissolved in a silicate slag. It is generally a batch process generating large amounts of SO_2 containing gases. In batch mode, the slag is poured several times. The slag returns to the matte smelting furnace (first step) to recover copper losses and the copper phase (called blister (~ 97%Cu) is further processed for refining processing.

[0006] There exist in scientific literature, patent and industrial practice, a large number of specific processes for the matte-blister route, including continuous matte smelting, iron free matte smelting (white metal production) or direct blister route. However in all of them sulphur is oxidized to SO_2 .

[0007] Electrochemical alternative methods have also been described in prior art for the converting of Copper.

[0008] Document "Anodic dissolution of copper sulphide ores in molten ZnCl_2 - KCl " published by Bertram et Al. in Trans. Instn. Min. Metall.(C: Mineral Process. Extr. Metall.) 1983, describes the anodic dissolution of copper sulphide ores in an eutectic mixture of ZnCl_2 and KCl . In this document, the temperature is maintained between about 300°C and 400°C , in order to avoid the vaporization of ZnCl_2 (boiling temperature of ZnCl_2 is around 732°C). At this temperature, both electrodes remain solids, which usually lead to dendritic growth at the cathode. This particular type of growth has several drawbacks, as the inclusion of electrolyte in the electrode, growing of needle shaped structures that can induce

short circuits and current instabilities, rendering industrial scale-up difficult.

[0009] The document US3326644 describes a process for the electrolytic deposition of copper from a molten salt electrolyte mixture. In this document, eutectic mixtures of chloride salts such as KCl/NaCl are used to minimize the cell temperature, which is comprised between 800 and 900°C . The copper deposit is in the form of intermeshed filaments having a "wool-like" appearance. This structure needs to be washed out with water before further processing in order to get rid of the salts which are trapped by capillary forces when getting the deposit out of the electrolyte.

Aims of the Invention

[0010] The present invention aims to provide a process for the production of copper from copper sulphide containing matte.

[0011] The present invention further aims to reduce the emission of pollutant such as SO_2 in the production process of copper from copper sulphide containing matte.

[0012] The present invention also aims to provide a process for the production of copper from copper sulphide containing matte wherein the sulphur by-products can be valued at least partly in its elemental chemical form.

[0013] The present invention further aims to provide copper in the liquid form, without the drawbacks of the solid deposit.

Summary of the Invention

[0014] The present invention discloses an anodic dissolution process at high temperature for the electrowinning of copper from a matte comprising Cu_2S , said process comprising the steps of:

- providing an electrolytic cell with a cathode container and an anode container;
- providing a molten copper cathode in said cathode container;
- providing a molten anode, comprising said metal matte in said anode container;
- providing an electrolyte comprising a molten salt;
- bringing said molten salt in contact with said cathode and said anode;
- applying a current to achieve electrolysis;
- recovering copper metal at the cathode.

[0015] According to particular preferred embodiments, the invention further discloses at least one or a suitable combination of the following features:

- the molten salt is selected from the group consisting of NaF , AlF_3 , CuCl and NaCl or mixing thereof;
- the raw material used for said molten salt is cryolithe;

- the anodic dissolution process generates elemental sulphur as a by-product at the anode;
- the process temperature is higher than copper melting temperature (1085°C).
- the recovered copper metal has a purity higher than 99%;
- precious metals of the group consisting of Ag, Au, Pt, Pd are recovered at the anode.
- heating is mainly obtained by the joule effect produced by electrolysis current;
- the process is performed continuously.

Brief Description of the Drawings

[0016] Fig. 1 represents a particular arrangement for an industrial electrolytic cell suitable for performing the production process of the present invention.

[0017] Fig. 2 represents the electrolytic cell arrangement of the example.

Detailed Description of the Invention

[0018] The basic step of the present invention is the conversion of copper sulphide containing matte into copper and elemental sulphur by electrolysis in fused salts, using liquid cathodes and anodes. Copper is produced at the cathode of a cell and refined afterwards if necessary by conventional methods used for blister copper. Sulphur is removed at the anode as a separate product, in its elemental form.

[0019] To achieve the process of the present invention, it is necessary to use temperatures above the melting temperature of both Cu_2S and metallic copper, so that the cathode is in the form of liquid copper, and the anode is in the form of liquid Sulphide copper (possibly containing other impurities, such as other metal sulphides). This has several advantages, such as the possibility to work at high current density and avoiding the appearance of spikes on the electrode surfaces. Those spikes producing particular inhomogeneous current densities, which can be detrimental to the process control. In the present invention, there is no need for a washing step as described in US3326644, the copper being directly drawn off from the cell in the liquid form, no impurities being included by capillary forces. In the same time, the sulphide compounds can be continuously fed in the molten anode, rendering the process particularly suitable for a continuous operation.

[0020] As the melting temperature of copper is higher than the vaporisation temperature of sulphur, sulphur escapes from the bath in gaseous form, avoiding the passivation of the anode which is the case with low temperature processes such as those in aqueous solution.

[0021] In a particular embodiment, the fused salt comprises a mixture of fluoride salts such as NaF and AlF_3 . A particular composition could be that of cryolite (Na_3AlF_6).

[0022] The process was further improved by the addi-

tion of chloride salts, such as NaCl and CuCl.

[0023] In a first embodiment of the present invention, the process is used for the recovery of copper from white metal. Said white metal is a matte almost free of iron. The white metal is first produced by a conventional method using state of the art pyrometallurgical processes. Then, the white metal 9 is fed into an anodic container, and said white metal is melted, forming a liquid anode 1. An electrolytic cell is used containing the fused salt 3 at the desired temperature, where copper from the anode 1 is dissolved by passing a direct current in the cell between the anode and the cathode 2. Liquid copper is deposited at the cathode 2. A continuous process is used essentially without external heating, the heating being produced by joule effect due to the electrolytic current. If necessary, for example at initial melting, additional heating can be provided by means of heater 7.

[0024] Undissolved impurities from the anode 1 such as precious metals (Ag, Au, Pt, Pd...) are additionally recovered from the anode 1.

[0025] Figure 1 represents a particular arrangement of an industrial electrolytic cell suitable for performing the process of the present invention. In this cell, the copper sulphide containing matte 9 is fed through an inlet at the liquid anode 1. This anode 1 is connected to the positive pole of a current source by means of an anode contact 4. On the other side, liquid copper forms the cathode 2, and is connected to the negative pole of the current source by means of a cathode contact 5. Both electrodes are separated by insulating refractory 6, the insulating refractory being suitable for being maintained in contact with the electrolyte at process temperature. For example, boron nitride or boron nitride coated parts could be used. The use of such materials can be limited to the walls being in contact with the electrolyte, the other walls being made out of standard refractory used in the pyrometallurgical process of copper sulphide. As current is injected through the cell, the anode 1 is consumed and copper, along with small amounts of some other impurities deposit on the cathode 2. The produced liquid copper is continuously taken out at an outlet. As the anode 1 is consumed, elemental sulphur is produced at the interface between the matte and the electrolyte, and escapes in gaseous form. This gaseous sulphur is then condensed and can be valued as such.

Example

[0026] A graphite crucible 10 of 4500 cm³ capacity, that acted as container and contact for a molten cathode 2, was filled with 6Kg of a salt mixture 3 of cryolite (60%Wt Na_3AlF_6) and sodium chloride (40%Wt NaCl), (See Fig. 2)

[0027] The crucible was heated in an induction furnace. The salt mixture was melted at 780°C.

[0028] An anode container 11 was fabricated in graphite to contain the liquid Cu_2S . Once the salt mixture was melted at 780 °C the anode container 11 filled up with

Cu₂S was completely immersed, the temperature was increased up to 1180 °C and the liquid Cu₂S anode 1 was 2cm under the electrolyte level. The surface of the liquid Cu₂S anode 1 in contact with the electrolyte was of 68 cm².

[0029] When the temperature was stabilized a potential of 2 V and a current of 100A was applied for 120 minutes. The current density calculated from the anode surface was 147 A/dm² and no anode effect was detected.

[0030] Once the electrolysis process was finished the anode container was removed from the bath and the casting of the overall melt (electrolyte + liquid copper) was made to allow cooling.

[0031] Metallic copper dispersed in the solid electrolyte and attached on the cathodic surface was recovered with a copper content higher than 99%.

[0032] An anodic dissolution of the anode was observed and quantified by lost weight. A current efficiency of 17% was calculated considering a Cu⁺¹ process. Elemental sulphur deposit was observed on cold free surfaces at the exit of the induction furnace.

Figure Keys

[0033]

1. Liquid anode (copper sulphide containing metal matte)
2. Liquid cathode (liquid copper blister)
3. Electrolyte
4. Anode contact
5. Cathode contact
6. Insulated refractory in electrolyte contact
7. Heating means
8. Copper outflow
9. Metal matte feeding
10. Graphite crucible
11. Graphite anode container

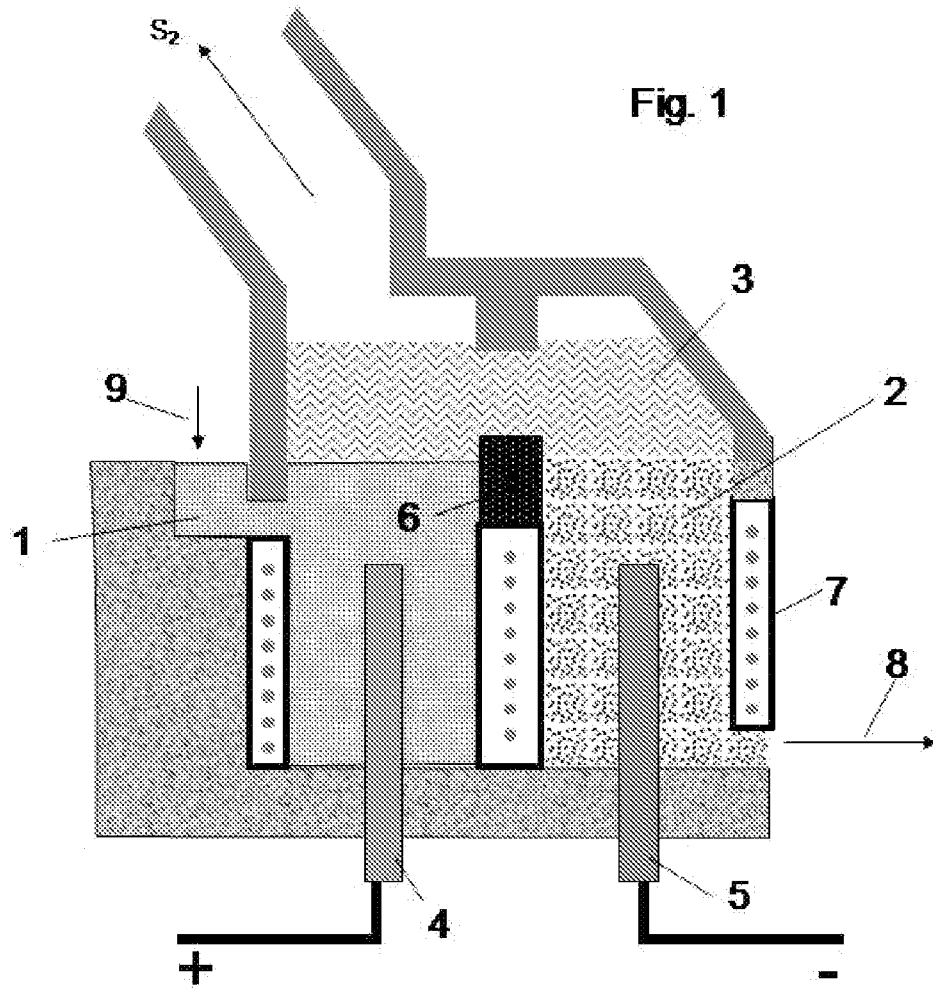
Claims

1. An anodic dissolution process at high temperature for the electrowinning of copper from a matte comprising Cu₂S, said process comprising the steps of:

- providing an electrolytic cell with a cathode container and an anode container;
- providing a molten copper cathode in said cathode container;
- providing a molten anode, comprising said metal matte in said anode container;
- providing an electrolyte comprising a molten salt;
- bringing said molten salt in contact with said cathode and said anode;
- applying a current to achieve electrolysis;

- recovering copper metal at the cathode.

2. The process of claim 1 wherein said molten salt is selected from the group consisting of NaF, AlF₃, NaCl and CuCl or mixing thereof.
3. The process of claim 2 wherein the raw material used for said molten salt is Cryolithe.
4. The process according to any of the previous claims wherein said process generates elemental sulphur as a by-product.
5. The process according to any of the previous claims wherein the temperature is higher than the copper melting temperature (1085°C).
6. The process according to any of the previous claims wherein recovered copper metal has a purity higher than 99%.
7. The process according to any of previous claims wherein precious metals selected from the group consisting of Ag, Au, Pt, Pd are recovered at the anode.
8. The process according to any of the previous claims wherein heating is obtained by the Joule effect produced by said current.
9. The process according to any of the previous claims **characterised in that** said process is performed continuously.



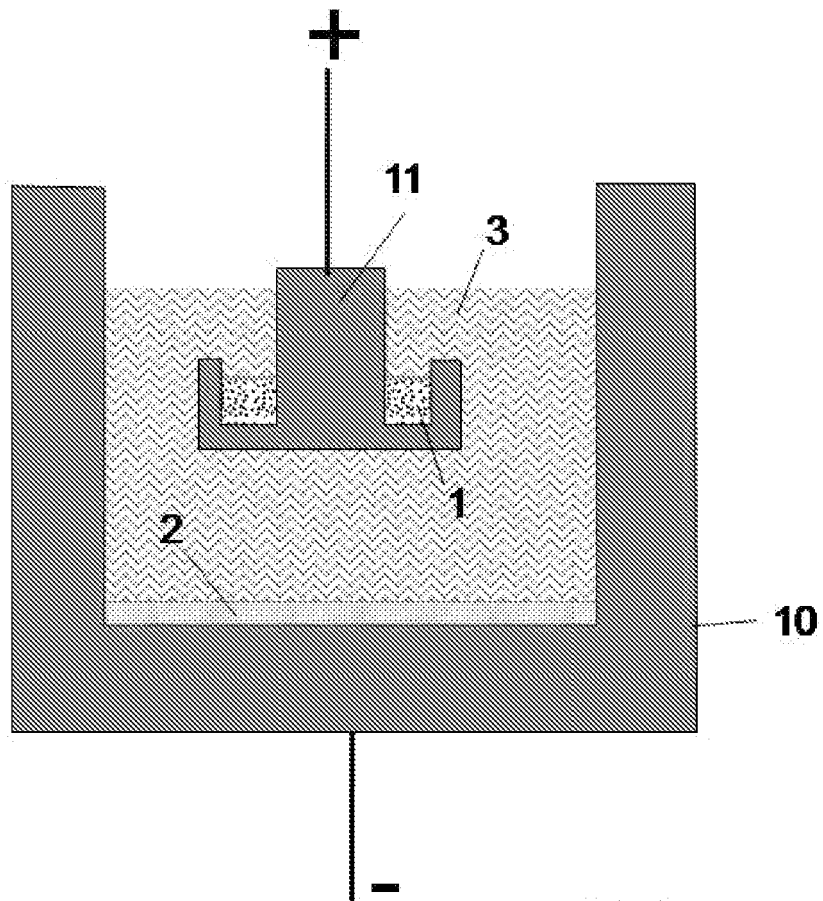


Fig.2



EUROPEAN SEARCH REPORT

Application Number
EP 08 16 0260

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 3 616 340 A (LAPAT PHILIP E) 26 October 1971 (1971-10-26) * column 2, line 65 - column 3, line 55 * * column 5, line 23 - column 6, line 9 * * column 13, lines 48-62 *	1-9	INV. C25C3/34
Y	-----	1-9	
Y,D	BERTRAM R ET AL: "Anodic dissolution of Copper Sulphide Ores in Molten ZnCl ₂ -KCl" TRANSACTIONS OF THE INSTITUTE OF MINING AND METALLURGY,, 1 January 1983 (1983-01-01), pages C169-C171, XP009109791 * the whole document *	1-9	
A	----- US 3 777 011 A (VELOSO A) 4 December 1973 (1973-12-04) * column 1, lines 49-53 * * column 2, lines 31-51 *	1-9	
A	----- US 4 405 415 A (DEWING ERNEST W [CA] ET AL) 20 September 1983 (1983-09-20) * claim 1; examples 1-5 *	1-9	TECHNICAL FIELDS SEARCHED (IPC) C25C
1 The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 10 December 2008	Examiner Hammerstein, G
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 08 16 0260

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

10-12-2008

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3616340 A	26-10-1971	NONE	

US 3777011 A	04-12-1973	NONE	

US 4405415 A	20-09-1983	AU 7605481 A	22-04-1982
		BR 8106445 A	22-06-1982
		EP 0049600 A1	14-04-1982
		ES 8302123 A1	01-04-1983
		JP 57092187 A	08-06-1982
		NO 813386 A	13-04-1982
		ZA 8106719 A	29-09-1982

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 3326644 A [0009] [0019]

Non-patent literature cited in the description

- **Bertram et al.** Anodic dissolution of copper sulphide ores in molten ZnCl₂-KCl. *Trans. Instn. Min. Metall.(C: Mineral Process. Extr. Metall.)*, 1983 [0008]